

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : NIPPON ESTER CO LTD

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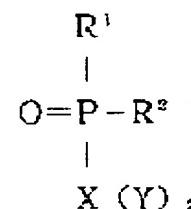
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MATSUMOTO TETSUO

## (54) FLAME-RESISTANT THERMOSET POLYESTER FILM

## (57)Abstract:

PURPOSE: To obtain an inexpensive product excellent in flame resistance, flexibility and meltproofness, etc., also generating no toxic gas in its contact with a flame, by three-dimensional crosslinking between a polyester resin with its main terminal being OH group and a specific organophosphorus compound using a specific curing agent.

CONSTITUTION: The objective product can be obtained by three-dimensional crosslinking between (A) a polyester resin with the main terminal being hydroxyl group and (B) an organophosphorus compound of the formula (R<sup>1</sup> and R<sup>2</sup> are each alkyl, aryl, etc.; X is trivalent organic group; Y is polyhydric (including monohydric) alcohol made up from aliphatic skeleton) [pref. diphenyl-(2,5-bis  $\beta$ -hydroxyethoxyphenyl)-phosphine oxide using (C) a curing agent reactive with hydroxyl group (pref. urethane-based curing agent such as  $\alpha$ -caprolactam-blocked isocyanate). It is preferable that this product be produced by uniformly sprinkling a substrate with powder of a thermosetting resin composition comprising the above components A, B and C followed by heat treatment to melt and crosslink the composition and by separating the resultant film from the substrate.



## LEGAL STATUS

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## \* NOTICES \*

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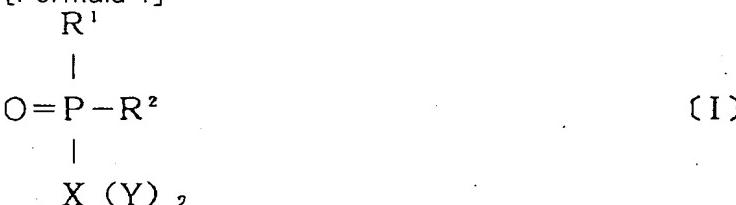
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## CLAIMS

## [Claim(s)]

[Claim 1] The polyester system flame resistance heat-curing film with which a main end consists of three components of the polyester resin which is a hydroxyl group, and the organic phosphorous compound and hydroxyl group which are expressed with the following general formula (1), and the curing agent which reacts and which carried out three-dimensions bridge formation.

[Formula 1]



(R1 and R2 are the congener or the radicals of a different kind which were chosen from the alkyl group, the aryl group, the alkoxy group, and the ant ROKISHI radical, and R1 and R2 may form the ring mutually.) Moreover, X is a trivalent organic radical and Y is alcohol more than the monovalence which consists of a frame of aliphatic series.

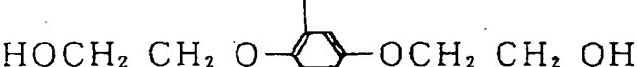
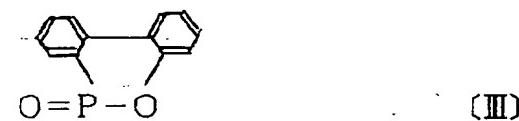
[Claim 2] The polyester system flame resistance heat-curing film according to claim 1 whose organic phosphorous compound expressed with a general formula (1) is a compound expressed with the following structure expression (2).

[Formula 2]



[Claim 3] The polyester system flame resistance heat-curing film according to claim 1 whose organic phosphorous compound expressed with a general formula (1) the main end of polyester resin is a hydroxyl group, and is a compound expressed with the following structure expression (3).

[Formula 3]



[Translation done.]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

## [0001]

[Industrial Application] This invention relates to the polyester system heat-curing film excellent in flame resistance, flexibility, dimensional stability, melting resistance, and chemical resistance.

## [0002]

[Description of the Prior Art] Conventionally, in the field of which flame resistance, such as an insulating film for motors and a flexible printed circuit board, flexibility, dimensional stability, melting resistance, chemical resistance, etc. are required, the film of thermoplastics, such as a general object for garments, polyester for industrial materials, and a polyamide, was not enough as these engine performance, and the service condition had a limit. Moreover, in high heat resistant resin, such as a polyether ether ketone and polyimide, there was a problem that cost was not high or a film moldability was not good etc.

[0003] Although the resin of bridge formation molds, such as thermosetting resin, is generally cheap and dimensional stability, melting resistance, and chemical resistance are also good, if it is made to harden, it will become weak and flexibility will no longer be acquired. In that respect, since the thermosetting resin constituent which consists of polyester resin and its curing agent contains the aromatic series component and the aliphatic series component moderately and after hardening has flexibility, film-izing is possible. And this film also has the description of the bridge formation mold resin of excelling also in dimensional stability, melting resistance, and chemical resistance. However, since many aliphatic series components are contained, flame resistance is not enough in essence, and grant of flame resistance is required.

[0004] Conventionally, the approach of using a tetrabromobisphenol A mold epoxy resin as a curing agent of polyester resin, the approach of copolymerizing the ethyleneoxide adduct of tetrabromobisphenol A in polyester resin, etc. are learned by flame resistance grant. However, by these approaches, there was a problem of generating the gas of a poisonous halogen system, at the time of \*\*\*\*.

## [0005]

[Problem(s) to be Solved by the Invention] This invention cancels the above faults, is cheap, is excellent also in flame resistance, flexibility, dimensional stability, melting resistance, and chemical resistance, and, moreover, offers the polyester system flame resistance heat-curing film which does not generate a toxic gas at the time of \*\*\*\*.

## [0006]

[Means for Solving the Problem] The polyester resin whose main end is a hydroxyl group as a result of this invention persons' repeating research wholeheartedly to such a situation about a polyester system flame resistance heat-curing film without the problem like the above, The heat-curing film which is obtained by stiffening the organic phosphorous compound which has two or more hydroxyl groups as a functional group using a hydroxyl group and the curing agent which reacts and which carried out three-dimensions bridge formation has flame resistance. And it found out that it was what may be satisfied also about flexibility, dimensional stability, melting resistance, and chemical resistance, and this invention was reached.

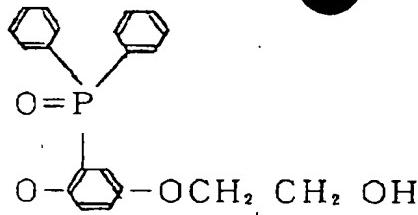
[0007] That is, the summary of this invention is as follows. It is the polyester system flame resistance heat-curing film with which a main end consists of three components of the polyester resin which is a hydroxyl group, and the organic phosphorous compound and hydroxyl group which are expressed with the following general formula (1), and the curing agent which reacts and which carried out three-dimensions bridge formation.

[Formula 1] (R1 and R2 are the congener or the radicals of a different kind which were chosen from the alkyl group, the aryl group, the alkoxy group, and the ant ROKISHI radical, and R1 and R2 may form the ring mutually.) Moreover, X is a trivalent organic radical and Y is alcohol more than the monovalence which consists of a frame of aliphatic series.

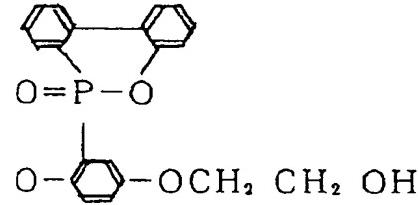
[0008] In this invention, the compound shown by the degree type as an organic phosphorous compound

expressed with a general formula (1) is mentioned.

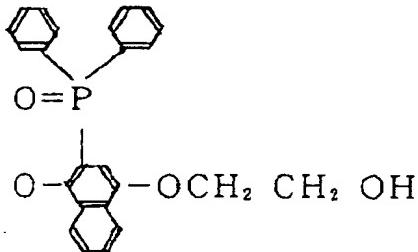
[Formula 4]



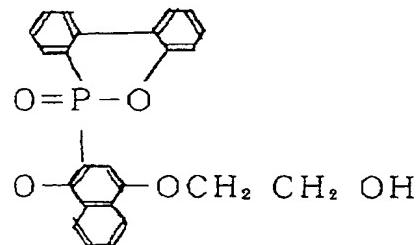
[Formula 5]



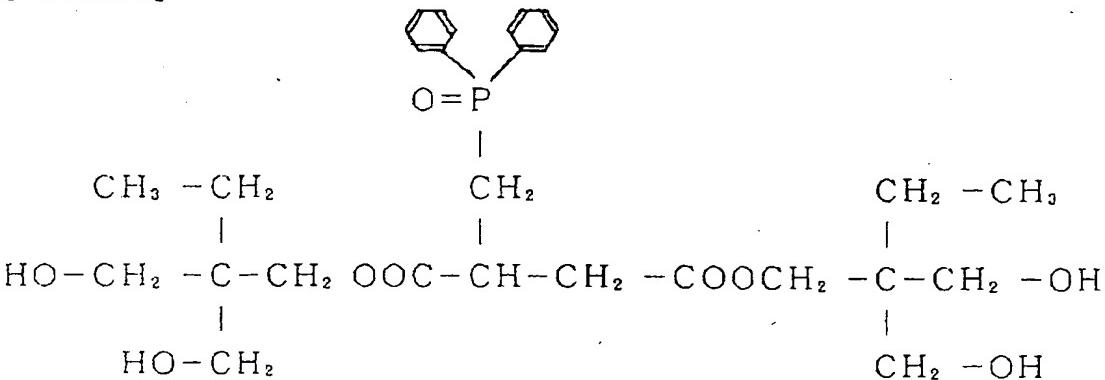
[Formula 6]



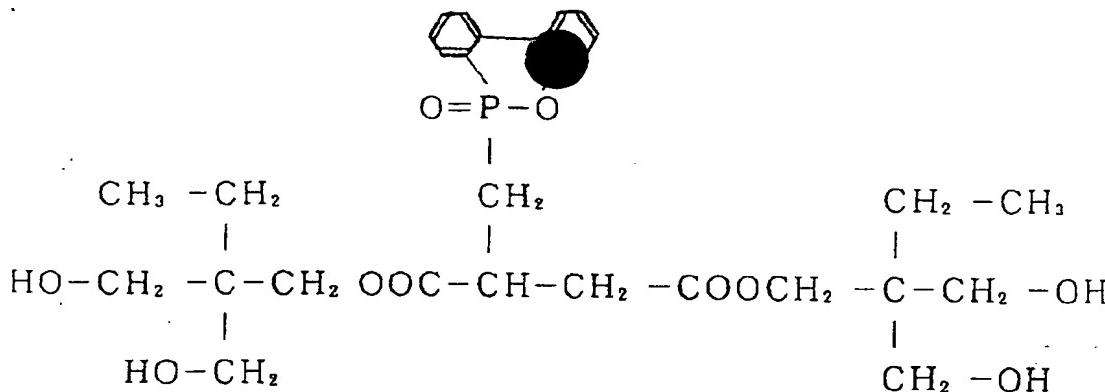
[Formula 7]



[Formula 8]



[Formula 9]



If volatilization of the stability of phosphorus compounds, the height of the Lynn atom content, and the phosphorus compounds in a film chemically-modified degree, the little of scattering, the effect of the flexibility on a film, etc. are synthetically judged also in these, [Formula 4] phosphorus-compounds diphenyl-(2, 5-bis-beta hydroxy ethoxy phenyl)-phosphine oxide come out of and shown -- or [Formula 5] The phosphorus compounds 9 come out of and shown, 10-dihydro-9-OKISA -10 -(2', 5' - bis-beta hydroxy ethoxy phenyl)- Phospho phenanthrene-10-oxide is desirable.

[0009] In this invention, the thing which makes a subject the thing which makes a subject aromatic series dicarboxylic acid, such as a terephthalic acid and isophthalic acid, as a dicarboxylic acid component as a constituent of polyester resin, and makes a subject aliphatic series diols, such as ethylene glycol and neopentyl glycol, as a diol component or dicarboxylic acid, diol, and hydroxy acid, or the thing which makes hydroxy acid a constituent is good, and there are a tartaric acid, a 4-hydroxybenzoic acid, etc. as hydroxy acid, for example. And since a melting fluidity and crosslinking reaction nature of that whose alcohol more than trivalence, such as a carboxylic acid more than trivalence, such as aliphatic series dicarboxylic acid, such as an adipic acid and an azelaic acid, trimellitic acid, and pyromellitic acid, trimethylol propane, and pentaerythritol, etc. is in these by little \*\*\*\* improve, it is more desirable.

[0010] Moreover, the average degree of polymerization of polyester resin has the desirable thing of the range of 5 – 50wt%. When what has polymerization degree lower than this is used as a film, sufficient reinforcement may not be obtained, or as for what has polymerization degree higher than this, film-ization may become difficult.

[0011] In this invention, the curing agent of an urethane system or a melamine system is desirable as a curing agent which stiffens polyester resin and an organic phosphorous compound. For example, as a curing agent of an urethane system, there is a methylation melamine (Cymel 303 by Mitsui Cyanamid and SUMIMARU M-100 by Sumitomo Chemical Co., Ltd.) etc. as epsilon caprolactam blocked isocyanate (Addukt[ by DAISERU Huels ] B-1530 and B-1065), and a melamine system curing agent.

[0012] in this invention, although the blending ratio of coal of polyester resin, an organic phosphorous compound, and a curing agent changes with the end group of polyester resin, the functional group of an organic phosphorous compound, and amounts of each functional group of a curing agent, the rate of polyester resin to the total amount of resin has the desirable range of 10 – 90wt%. If the flexibility of a film is inferior if there are few rates of polyester resin than this, or the rate of polyester resin increases more than this, the flame resistance of a film and thermal resistance may fall.

[0013] Next, the rate of an organic phosphorous compound to the total amount of resin has the desirable range of 5 – 40wt%. If there are few rates of an organic phosphorous compound than this, the flame resistance of a film may be inferior, or if the rate of an organic phosphorous compound increases more than this, the thermal resistance and chemical resistance of a film may fall.

[0014] Next, what is necessary is just to blend a curing agent so that the total amount of the end group of polyester resin and the functional group of an organic phosphorous compound and the amount of functional groups of a curing agent may be set to 1:1. Specifically, the rate of a curing agent to the total amount of resin has the desirable range of 5 – 50wt%. If there are few rates of a curing agent than this, thermal resistance may not be enough, or if the rate of a curing agent increases more than this, flexibility may fall.

[0015] Although the film of this invention fabricates polyester resin, an organic phosphorous compound and a curing agent, and the other resin constituents that blended hardening accelerators, additives, etc., such as the third class amine and an organometallic complex, if needed in the shape of a film and should just stiffen this, its approach of the point of obtaining advantageously industrially to a degree is desirable.

[0016] That is, it is the approach of a thermosetting resin constituent carrying out a melting flow of this base material, and making a bridge constructing while carrying out melting of the thermosetting resin constituent by

heat-treating substantially above the temperature in which a hardening reaction is possible, considering as the shape of a film, separating a base material and a film, and obtaining a heat-curing film after grinding a thermosetting resin constituent in the shape of powder and sprinkling this to homogeneity on a base material. In fact, grinding of a thermosetting resin constituent is good for setting particle size to 50 micrometers or less to make it 30 micrometers or less often and more preferably. If it becomes larger than this, a film front face becomes coarse and smooth nature may be spoiled. Since fine particles with uniform a ball mill grinding in grinding the thermosetting resin constituent which fully carried out cooling solidification are obtained, it is desirable.

[0017] Next, although spraying of a up to [ the base material of a thermosetting resin constituent ] should just sprinkle the fine particles of the ground thermosetting resin constituent to homogeneity on base materials, such as a metal or resin, it electrifies static electricity in the fine particles of the thermosetting resin constituent ground more preferably, sprinkles this on a metal plate, and can be carried out to that the method of making fine particles adsorb on the surface of a plate in an operation of static electricity is simple, and homogeneity. And since it is adsorption by static electricity, the fine particles of a thermosetting resin constituent can be made to be able to stick to the thing of the configuration of arbitration by the thickness of arbitration, therefore the heat-curing film of the configuration of arbitration can be manufactured. Moreover, the thickness of a film is easily controllable by adjusting the amount of the thermosetting resin constituent distributed on a base material. In addition, in order to improve the separability of a film, as for the front face of a metal plate, it is desirable to process by the release agent of a fluorine system or a silicon system.

[0018] About heat treatment, it carries out in a homothermal furnace, and a thermosetting resin constituent carries out a melting flow, and it carries out substantially above the temperature in which a hardening reaction is possible. Moreover, the separation from the base material of a film can separate the film which heat-hardened easily by exfoliating from a base material.

[0019]

[Function] In this invention, although it is cheap and being excelled in flexibility, dimensional stability, melting resistance, and chemical resistance, the polyester resin whose main end is a hydroxyl group, and the organic phosphorous compound which has two or more hydroxyl groups as a functional group are stiffened using a hydroxyl group and the curing agent which reacts about the polyester system heat-curing film with which the problem of being bad has flame resistance. Therefore, the three-dimensions structure of cross linkage which consists of three components of polyester resin, an organic phosphorous compound, and a curing agent is made, and flame resistance is given by introducing the Lynn atom into a film. Since this organic phosphorous compound has aliphatic series in that frame, even if it is introduced into the structure of cross linkage, the flexibility of a film is not spoiled and it decomposes at the time of \*\*\*\*, and it forms the protective coat of the phosphoric acid of a non-volatile, and discovers flame resistance by promoting carbonization of the organic substance by the dehydrating action of the phosphoric acid which generated, forming a carbonization coat, and intercepting supply of oxygen.

[0020]

[Example] Next, an example explains this invention concretely. In addition, the measurement of the characteristic value in an example is as follows.

Flame resistance flame resistance was judged by the film appraisal method by UL-94 specification. Strong ductility Oriental Baldwin tensilon UTM-4-100 mold is used, and it is a 1cmx10cm piece of a film 10 cm/min The tension test was performed at the rate and it asked for the reinforcement of the point which the film fractured, and ductility.

Contraction of the film after leaving it for 10 minutes in hot air drying equipment with a rate [ of a heat shrink ] of 200 degrees C was measured.

It saw whether a flexible film would be bent and fractured. What is not fractured was made into O and what was fractured was made into x.

The smooth degree of a smooth nature film front face was judged visually. O and a little coarse thing were made into \*\*, and the coarse thing was made into x for the smooth thing.

The alkali-proof film was immersed for 60 minutes into 80-degree C 5%NaOH water solution, and the retention of breaking strength was measured. Retention made x O and 90% or less of thing for 90% or more of thing.

The hole was seen whether contact the tobacco with which fire arrived at the melting-resistant film for 5 seconds, and open. That in which a hole did not open was made into O, and what opened was made into x.

[0021] The copolymerized polyester resin 44 weight section, the epsilon caprolactam blocked isocyanate (Addukt [ by DAISERU Huels ] B-1530) 33 weight section whose average degree of polymerization which consists of trimethylol propane 4mol% as a trivalent glycol ethylene glycol 36mol% neopentyl glycol 60mol% as a terephthalic acid and a diol component as an example 1 dicarboxylic-acid component is 25 and whose end hydroxyl values

are 550geq(s) / 106g, [Formula 4] After coming out and carrying out the dryblend of the organic phosphorous compound 23 weight section shown, the hardening-accelerator (Sankyo Organic Chemicals Stann OMF) 0.2 weight section, and the flowing agent (Acronal 4 by BASF A.G. F) 0.7 weight section with a Henschel mixer (Mitsui Miike factory FM10B mold), melting kneading was carried out at 120 degrees C using the KO kneader (PR-46 made from BUSSU mold), the ball mill after cooling solidification ground, the wire gauze of 145 meshes separated, and fine particles were obtained. Using the electrostatic-coating machine for paint, these fine particles were sprinkled so that thickness might be set to 75 micrometers on a steel plate. This steel plate was heat-treated in 20-minute hot air drying equipment at 190 degrees C. In addition, the front face of a steel plate washed dust, fats and oils, etc. beforehand, and applied the fluorine system release agent (die free-lancer by Daikin, LTD.). After cooling the heat-treated steel plate to a room temperature in air, the film was stripped from the steel plate and the heat-curing film was obtained. The physical properties of the obtained film are shown in Table 1. It had the flame resistance which was excellent since this film has flexibility and the Lynn atom was contained.

[0022] As example 2 organic phosphorous compound [Formula 5] It carried out like the example 1 except having come out and having used what is shown. The physical properties of the obtained film are shown in Table 1. It had the flame resistance which was excellent since this film also has flexibility and the Lynn atom was contained.

[0023] The copolymerized polyester resin 45 weight section, the methylation melamine (SUMIMARU M-100 by Sumitomo Chemical Co., Ltd.) 34 weight section which were used in the example 3 example 1, [Formula 4] It came out and carried out like the example 1 using the organic phosphorous compound 21 weight section and the flowing agent (Acronal 4 by BASF A.G. F) 0.7 weight section which are shown. The physical properties of the obtained film are shown in Table 1. Like [ this film ] the example 1, there is flexibility and it had the outstanding flame resistance.

[0024] It carried out like the example 1 using the copolymerized polyester resin 87 weight section used in the example of comparison 1 example 1, the epsilon caprolactam blocked isocyanate (Addukt[ by DAISERU Huels ] B-1530) 13 weight section, the hardening-accelerator (Sankyo Organic Chemicals Stann OMF) 0.2 weight section, and the flowing agent (Acronal 4 by BASF A.G. F) 0.7 weight section. The physical properties of the obtained film are shown in Table 1. Although flexibility was good, since this film did not contain the Lynn atom, it became that in which flame resistance does not have self-extinguishing bad, either.

[0025] The film was obtained like the example 1 using the copolymerized polyester resin 86 weight section of the end hydroxyl-group mold used in the example of comparison 2 example 1, the methylation melamine (SUMIMARU M-100 by Sumitomo Chemical Co., Ltd.) 14 weight section, and the flowing agent (Acronal 4 by BASF A.G. F) 0.7 weight section. The physical properties of the obtained film are shown in Table 1. This film of flexibility was good, and since the Lynn atom was not contained, flame resistance also became what does not have self-extinguishing bad.

[0026]

[Table 1]

	破断強度 (MPa)	破断伸度 %	熱収縮率 %	耐炎 UL-94	可撓性	平滑性	耐アルカリ性	防融性
実施例1	112.4	3.5	0.2	VTM=0	○	○	○	○
実施例2	110.9	3.5	0.2	VTM=0	○	○	○	○
実施例3	112.6	2.9	0.1	VTM=0	○	○	○	○
比較例1	114.8	3.7	0.2	VTM=2 未満	○	○	○	○
比較例2	113.1	3.0	0.1	VTM=2 未満	○	○	○	○

[0027]

[Effect of the Invention] This invention is cheap, it excels also in dimensional stability, melting resistance, and alkali resistance, moreover flame resistance and flexibility are satisfied, and the heat-curing film which does not generate a toxic gas at the time of \*\*\* is offered.

[Translation done.]

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3/24	CFD Z	9268-4F		
C 08 K 5/53	KKD	7242-4J		
C 08 L 67/02	LPK	8933-4J		

審査請求 未請求 請求項の数3(全6頁)

(21)出願番号	特願平4-345487	(71)出願人	000228073 日本エステル株式会社 愛知県岡崎市日名北町4番地1
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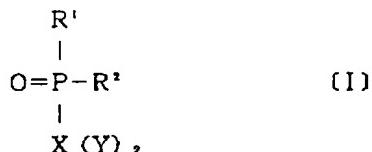
(54)【発明の名称】 ポリエステル系耐炎性熱硬化フィルム

(57)【要約】

【目的】 安価で耐炎性、可撓性、寸法安定性、防融性、耐薬品性に優れ、しかも接炎時に有毒ガスを発生することのないポリエステル系耐炎性熱硬化フィルムを得る。

【構成】 主たる末端が水酸基であるポリエステル樹脂と、下記一般式(I)で表される有機りん化合物および水酸基と反応する硬化剤の三成分からなる三次元架橋したポリエステル系耐炎性熱硬化フィルム。

【化1】



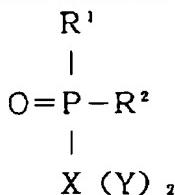
(R<sup>1</sup>、R<sup>2</sup>はアルキル基、アリール基、アルコキシ基及びアリロキシ基から選ばれた同種または異種の基であり、R<sup>1</sup>、R<sup>2</sup>は互いに環を形成してもよい。また、Xは三価の有機基であり、Yは脂肪族の骨格からなる一価以上のアルコールである。)

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## 【特許請求の範囲】

【請求項1】主たる末端が水酸基であるポリエステル樹脂と、下記一般式(1)で表される有機リン化合物および\*



(R<sup>1</sup>、R<sup>2</sup>はアルキル基、アリール基、アルコキシ基、及びアリロキシ基から選ばれた同種または異種の基であり、R<sup>1</sup>、R<sup>2</sup>は互いに環を形成していてもよい。また、Xは三価の有機基であり、Yは脂肪族の骨格からなる一価以上のアルコールである。)

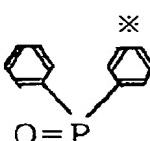
\* び水酸基と反応する硬化剤の三成分からなる三次元架橋したポリエステル系耐炎性熱硬化フィルム。

## 【化1】

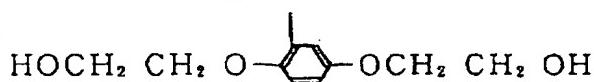
(I)

10※【請求項2】一般式(1)で表される有機リン化合物が下記構造式(2)で表される化合物である請求項1記載のポリエステル系耐炎性熱硬化フィルム。

## 【化2】

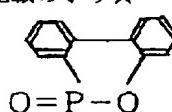


(II)

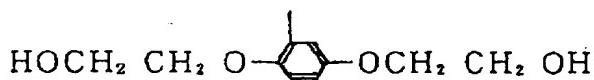


★エスチル系耐炎性熱硬化フィルム。

## 【化3】



(III)



## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、耐炎性、可撓性、寸法安定性、防融性、耐薬品性にすぐれたポリエステル系熱硬化フィルムに関するものである。

## 【0002】

【従来の技術】従来、モーター用絶縁フィルムやフレキシブルプリント基板等の耐炎性、可撓性、寸法安定性、防融性、耐薬品性等を要求される分野では、一般的衣料用、産業資材用ポリエステルやポリアミド等の熱可塑性樹脂のフィルムではこれらの性能が十分でなく、使用条件に制限があった。また、ポリエーテルエーテルケトンやポリイミド等の高耐熱性樹脂ではコストが高かったり、フィルム成形性がよくなかったりする等の問題があった。

【0003】熱硬化性樹脂等の架橋型の樹脂は、一般に安価で寸法安定性、防融性、耐薬品性もよいが、硬化させると脆くなってしまって可撓性が得られなくなる。その点、ポリエステル樹脂とその硬化剤からなる熱硬化性樹脂組成物は芳香族成分と脂肪族成分を適度に含有しており、硬化後も可撓性を有しているのでフィルム化が可能であ

る。そして、このフィルムは、寸法安定性、防融性、耐薬品性にも優れているという架橋型樹脂の特徴も有している。しかし、脂肪族成分を多く含有しているので本質的に耐炎性が十分でなく、耐炎性の付与が必要である。

【0004】従来、耐炎性付与には、テトラブロモビスフェノールA型エボキシ樹脂をポリエステル樹脂の硬化剤として用いる方法や、テトラブロモビスフェノールAのエチレンオキサイド付加体をポリエステル樹脂に共重合する方法等が知られている。しかし、これらの方法では、接炎時に有毒なハロゲン系のガスを発生するという問題があった。

## 【0005】

【発明が解決しようとする課題】本発明は、上記のような欠点を解消し、安価で耐炎性、可撓性、寸法安定性、防融性、耐薬品性にも優れ、しかも、接炎時に有毒ガスを発生することのないポリエステル系耐炎性熱硬化フィルムを提供するものである。

## 【0006】

【課題を解決するための手段】本発明者らは、このような状況に対して、上記のごとき問題のないポリエステル系耐炎性熱硬化フィルムについて鋭意研究を重ねた結果

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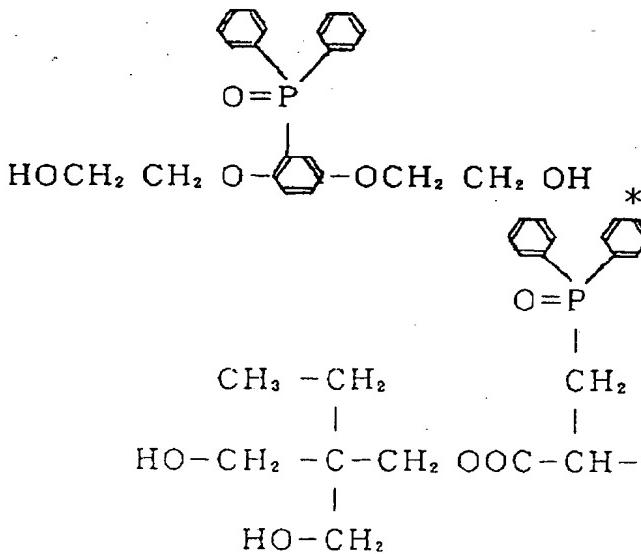
果、主たる末端が水酸基であるポリエステル樹脂と、二個以上の水酸基を官能基として有する有機リン化合物とを、水酸基と反応する硬化剤を用いて硬化させることにより得られる三次元架橋した熱硬化フィルムが耐炎性を有し、かつ、可撓性、寸法安定性、防融性、耐薬品性についても満足し得るものであることを見いだし本発明に到達した。

〔0007〕すなわち、本発明の要旨は次のとおりである。主たる末端が水酸基であるポリエステル樹脂と、下記一般式(1)で表される有機リン化合物および水酸基と反応する硬化剤の三成分からなる三次元架橋したポリエステル系耐炎性熱硬化フィルムである。

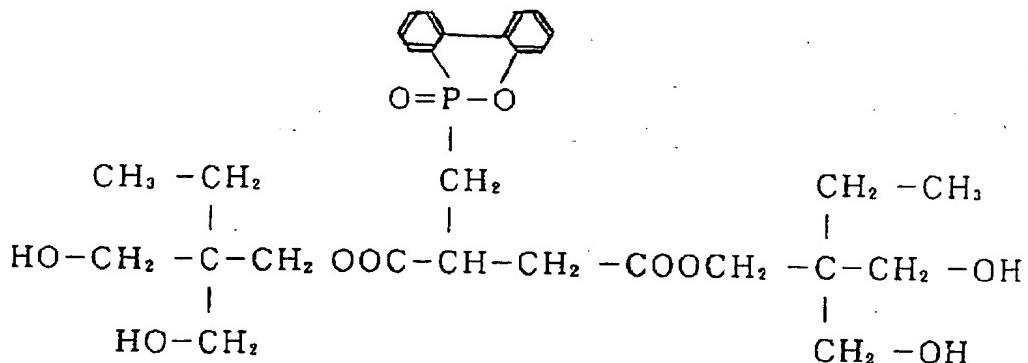
〔化1〕 ( $R^1$ 、 $R^2$  はアルキル基、アリール基、アルコキシ基、及びアリロキシ基から選ばれた同種または異種の基であり、 $R^1$ 、 $R^2$  は互いに環を形成していてもよい。また、Xは三価の有機基であり、Yは脂肪族の骨格からなる一価以上のアルコールである。)

〔0008〕本発明において、一般式(1)で表される有機リン化合物としては次式で示される化合物が挙げられる。

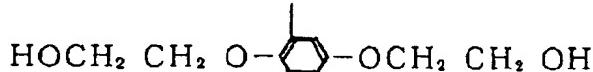
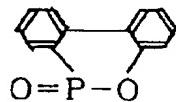
[化4]



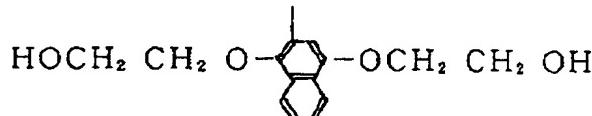
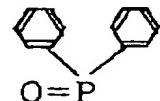
〔化9〕



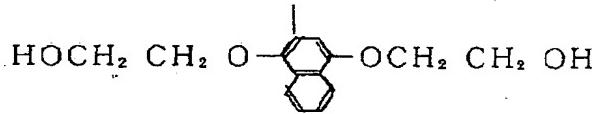
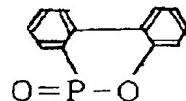
\* (化5)



【化6】



〔化7〕



【化8】

これらのなかでも、リン化合物の安定性、リン原子含有率の高さ、フィルム化工程でのリン化合物の揮発、飛散の少なさ、フィルムの可撓性への影響等を総合的に判断すると、

【化4】で示されるリン化合物ジフェニル-(2,5-ビス $\beta$ -ヒドロキシエトキシフェニル)-ホスフィンオキシド、または、

【化5】で示されるリン化合物9,10-ジヒドロ-9-オキサ-10-(2',5'-ビス $\beta$ -ヒドロキシエトキシフェニル)-ホスファフェナントレン-10-オキシドが好ましい。

【0009】本発明において、ポリエステル樹脂の構成成分としてはジカルボン酸成分としてテレフタル酸、イソフタル酸等の芳香族ジカルボン酸を主体とし、ジオール成分としてエチレングリコール、ネオベンチルグリコール等の脂肪族ジオールを主体とするもの、あるいはジカルボン酸、ジオールおよびオキシカルボン酸を主体とするもの、あるいはオキシカルボン酸を構成成分とするものがよく、オキシカルボン酸としては、例えば、酒石酸や4-ヒドロキシ安息香酸等がある。そして、これらにアジピン酸やアゼライン酸等の脂肪族ジカルボン酸、トリメリット酸やビロメリット酸等の三価以上のカルボン酸、トリメチロールプロパン、ペントエリスリトール等の三価以上のアルコール等を少量含んでいるものは溶融流動性、架橋反応性が向上するのでより好ましい。

【0010】また、ポリエステル樹脂の平均重合度は5~50wt%の範囲のものが好ましい。これより重合度が低いものはフィルムにしたとき十分な強度が得られなかったり、これより重合度が高いものはフィルム化が困難になる場合がある。

【0011】本発明において、ポリエステル樹脂と有機リン化合物とを硬化させる硬化剤としては、ウレタン系やメラミン系の硬化剤が好ましい。例えば、ウレタン系の硬化剤としては $\epsilon$ -カブロラクタムブロックドイソシアナート(ダイセルヒュルス社製Addukt B-1530やB-1065)、また、メラミン系硬化剤としてはメチル化メラミン(三井サイアナミッド社製サイメル303や住友化学社製スミマールM-100)等がある。

【0012】本発明において、ポリエステル樹脂、有機リン化合物、硬化剤の配合割合は、ポリエステル樹脂の末端基、有機リン化合物の官能基、硬化剤の官能基各々の量により異なるが、全樹脂量に対するポリエステル樹脂の割合は10~90wt%の範囲が好ましい。ポリエステル樹脂の割合がこれより少ないとフィルムの可撓性が劣ったり、ポリエステル樹脂の割合がこれより多くなるとフィルムの耐炎性や耐熱性が低下する場合がある。

【0013】次に、全樹脂量に対する有機リン化合物の割合は5~40wt%の範囲が好ましい。有機リン化合物の割合がこれより少ないとフィルムの耐炎性が劣った

り、有機リン化合物の割合がこれより多くなるとフィルムの耐熱性や耐薬品性が低下したりする場合がある。

【0014】次に、硬化剤は、ポリエステル樹脂の末端基と有機リン化合物の官能基の総量と硬化剤の官能基量が1:1となるように配合すればよい。具体的には、全樹脂量に対する硬化剤の割合は5~50wt%の範囲が好ましい。硬化剤の割合がこれより少ないと耐熱性が十分でなかったり、硬化剤の割合がこれより多くなると可撓性が低下したりする場合がある。

【0015】本発明のフィルムは、ポリエステル樹脂と有機リン化合物および硬化剤、その他必要に応じて三級アミンや有機金属錯体等の硬化促進剤や添加剤等を配合した樹脂組成物をフィルム状に形成し、これを硬化させればよいのであるが、工業的に有利に得るという点から次の方法が好ましい。

【0016】すなわち、熱硬化性樹脂組成物を粉末状に粉碎し、これを基材上に均一に散布した後、この基材を熱硬化性樹脂組成物が溶融流動し、かつ実質的に硬化反応が可能な温度以上で熱処理することにより熱硬化性樹脂組成物を溶融させるとともに架橋させてフィルム状とし、基材とフィルムを分離して熱硬化フィルムを得る方法である。実際には、熱硬化性樹脂組成物の粉碎は粒径を50μm以下にするのがよく、より好ましくは30μm以下にするのがよい。これより大きくなるとフィルム表面が粗くなり平滑性が損なわれる場合がある。粉碎には、十分に冷却固化した熱硬化性樹脂組成物をボールミルで粉碎するのが均一な粉体が得られるので好ましい。

【0017】次に、熱硬化性樹脂組成物の基材上への散布は、粉碎した熱硬化性樹脂組成物の粉体を金属または樹脂等の基材上に均一に散布すればよいのであるが、より好ましくは粉碎した熱硬化性樹脂組成物の粉体に静電気を帯電させ、これを金属製の板上に散布し、静電気の作用で粉体を板の表面に吸着させる方法が簡便かつ均一に行える。しかも静電気による吸着であるので、任意の形状のものに、任意の厚さで熱硬化性樹脂組成物の粉体を吸着させることができ、従って任意の形状の熱硬化フィルムを製造することができる。また、基材上に分散させる熱硬化性樹脂組成物の量を加減することにより容易にフィルムの厚さを制御できる。なお、金属製の板の表面はフィルムの分離性をよくするためにフッ素系またはシリコン系の離型剤で処理しておくのが好ましい。

【0018】熱処理については、恒温の炉の中で行い、熱硬化性樹脂組成物が溶融流動し、かつ実質的に硬化反応が可能な温度以上で行う。また、フィルムの基材からの分離は、熱硬化したフィルムを基材から剥離することにより簡単に分離できる。

【0019】

【作用】本発明は、安価で可撓性、寸法安定性、防融性、耐薬品性等には優れているが、耐炎性が悪いという問題のあるポリエステル系熱硬化フィルムについて、主

たる末端が水酸基であるポリエステル樹脂と二個以上の水酸基を官能基として有する有機リン化合物と、水酸基と反応する硬化剤を用いて硬化させることにより、ポリエステル樹脂、有機リン化合物、硬化剤の三成分からなる三次元架橋構造を作り、フィルム中にリン原子を導入することにより耐炎性を付与したものである。この有機リン化合物は、その骨格に脂肪族を有しているので架橋構造中に導入されてもフィルムの可撓性を損なうことなく、また、接炎時には分解して不揮発性のリン酸の保護膜を形成し、そして、生成したリン酸の脱水作用により有機物の炭化を促進して炭化被膜を形成し、酸素の供給を遮断することにより耐炎性を発現するものである。

## 【0020】

【実施例】次に実施例によって本発明を具体的に説明する。なお、実施例中の特性値の測定は次の通りである。

## 耐炎性

耐炎性は、UL-94規格によるフィルム評価法により判定した。

## 強伸度

東洋ポールドウイン社製テンシロンUTM-4-100型を用い、1cm×10cmのフィルム片を10cm/minの速度にて引張試験を行い、フィルムが破断した点の強度、伸度を求めた。

## 熱収縮率

200°Cの熱風乾燥機中に10分間放置した後のフィルムの収縮率を測定した。

## 可撓性

フィルムを折り曲げて破断するかどうかをみた。破断しないものを○、破断したものを×とした。

## 平滑性

フィルム表面の平滑度合を目視にて判定した。平滑なものを○、やや粗いものを△、粗いものを×とした。

## 耐アルカリ性

フィルムを80°Cの5%NaOH水溶液中に60分間浸漬して、破断強度の保持率を測定した。保持率が90%以上のものを○、90%以下のものを×とした。

## 防融性

フィルムに火の着いたタバコを5秒間接触させ穴があくかどうかをみた。穴のあかなかつたものを○、あいたものを×とした。

## 【0021】実施例1

ジカルボン酸成分としてテレフタル酸、ジオール成分としてエチレングリコール36m o 1%ネオペンチルグリコール60m o 1%、三価のグリコールとしてトリメチロールプロパン4m o 1%からなる平均重合度が2.5、末端水酸基価が55.0 geq / 10gである共重合ポリエステル樹脂44重量部、ε-カブロラクタムブロックドイソシアナート（ダイセルヒュルス社製Addukt B-1530）13重量部、硬化促進剤（三共有機合成社製Stann OM F）0.2重量部、流展剤（BASF社製アクロナール4F）0.7重量部をヘンシェルミキサー（三井三池製作所製FM10B型）でドライブレンドした後、コ・ニーダー（ブッス社製PR-46型）を用いて120°Cで溶融混練し、冷却固化後ポールミルにて粉碎し、145メッシュの金網で分離して粉体を得た。この粉体を塗装用の静電塗装機を用いて、鋼板上に膜厚が75μmになるように散布した。この鋼板を190°Cで20分熱風乾燥機中で熱処理した。なお、鋼板の表面はあらかじめゴミ、油脂等を洗净し、フッ素系離型剤（ダイキン社製ダイフリー）を塗布した。熱処理した鋼板を空気中で室温まで冷却した後、鋼板からフィルムをはがして熱硬化フィルムを得た。得られたフィルムの物性を表1に示す。このフィルムは可撓性があり、また、リン原子を含有しているので優れた耐炎性を有していた。

【化4】で示される有機リン化合物23重量部、硬化促進剤（三共有機合成社製Stann OM F）0.2重量部、流展剤（BASF社製アクロナール4F）0.7重量部をヘンシェルミキサー（三井三池製作所製FM10B型）でドライブレンドした後、コ・ニーダー（ブッス社製PR-46型）を用いて120°Cで溶融混練し、冷却固化後ポールミルにて粉碎し、145メッシュの金網で分離して粉体を得た。この粉体を塗装用の静電塗装機を用いて、鋼板上に膜厚が75μmになるように散布した。この鋼板を190°Cで20分熱風乾燥機中で熱処理した。なお、鋼板の表面はあらかじめゴミ、油脂等を洗净し、フッ素系離型剤（ダイキン社製ダイフリー）を塗布した。熱処理した鋼板を空気中で室温まで冷却した後、鋼板からフィルムをはがして熱硬化フィルムを得た。得られたフィルムの物性を表1に示す。このフィルムは可撓性があり、また、リン原子を含有しているので優れた耐炎性を有していた。

## 【0022】実施例2

## 有機リン化合物として

【化5】で示されるものを用いた以外は実施例1と同様にして行った。得られたフィルムの物性を表1に示す。このフィルムも可撓性があり、また、リン原子を含有しているので優れた耐炎性を有していた。

## 【0023】実施例3

実施例1で用いた共重合ポリエステル樹脂45重量部、メチル化メラミン（住友化学社製スマーマルM-100）34重量部、

【化4】で示される有機リン化合物21重量部、流展剤（BASF社製アクロナール4F）0.7重量部を用いて実施例1と同様にして行った。得られたフィルムの物性を表1に示す。このフィルムも実施例1と同様に、可撓性があり、また、優れた耐炎性を有していた。

## 【0024】比較例1

実施例1で用いた共重合ポリエステル樹脂87重量部、ε-カブロラクタムブロックドイソシアナート（ダイセルヒュルス社製Addukt B-1530）13重量部、硬化促進剤（三共有機合成社製Stann OM F）0.2重量部、流展剤（BASF社製アクロナール4F）0.7重量部を用いて実施例1と同様にして行った。得られたフィルムの物性を表1に示す。このフィルムは可撓性は良いが、リン原子を含有していないので耐炎性も悪く自己消火性の無いものとなった。

## 【0025】比較例2

実施例1で用いた末端水酸基型の共重合ポリエステル樹脂86重量部、メチル化メラミン（住友化学社製スマーマルM-100）14重量部、流展剤（BASF社製アクロナール4F）0.7重量部を用いて実施例1と同様にしてフィルムを得た。得られたフィルムの物性を表1に示す。このフィルムも可撓性は良いが、リン原子を含有していないので耐炎性も悪く自己消火性の無いものと

なった。

[0026]

\*【表1】  
\*

	破断強度 (MPa)	破断伸度 %	熱収縮率 %	耐炎性 UL-94	可撓性	平滑性	耐アルカリ性	防融性
実施例1	112.4	3.5	0.2	VTM=0	○	○	○	○
実施例2	110.9	3.5	0.2	VTM=0	○	○	○	○
実施例3	112.6	2.9	0.1	VTM=0	○	○	○	○
比較例1	114.8	3.7	0.2	VTM=2 未満	○	○	○	○
比較例2	113.1	3.0	0.1	VTM=2 未満	○	○	○	○

[0027]

【発明の効果】本発明は、安価で寸法安定性、防融性、耐アルカリ性にも優れ、しかも耐炎性、可撓性共に満足

し、接炎時に有毒ガスを発生しない熱硬化フィルムが提供される。

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